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Synthesis and Characterization of BiCaSrCuO and  
BiSnCaSrCuO Superconducting Ceramics

by

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SYNTHESIS AND CHARACTERIZATION OF BiCaSrCuO AND  
BiSnCaSrCuO SUPERCONDUCTING CERAMICS

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Abstract Magnetic susceptibility measurements,  
resistance measurements, Rutherford backscattering,  
scanning electron microscopy, and energy dispersive  
X-ray analyses were utilized in order to determine the  
effects of composition and firing conditions on the  
properties of the Bi-Ca-Sr-Cu-O superconducting  
ceramics.

INTRODUCTION

New high - temperature superconducting materials with  $T_c$ 's  
in the range of 120K have recently been realized in both  
the Tl-Ca-Ba-Cu-O<sup>1</sup> and Bi-Ca-Sr-Cu-O<sup>2</sup> systems. These  
systems consist of at least two superconducting phases  
characterized by their superconducting transition  
temperatures of ~80K and ~120K. The transition  
temperature, critical current density, anisotropic  
properties, and volume fraction of the superconducting



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material are inherently related to the microstructure of the ceramics. In this report, we have investigated the effects of starting composition, Sn doping, and annealing and sintering conditions on the magnetic and electrical properties, microstructure, surface stoichiometry, and multiphasic nature of the Bi-Ca-Sr-Cu-O system.

#### EXPERIMENTAL

##### Synthesis

Samples of the Bi-Ca-Sr-Cu-O ceramics were synthesized via intimate mixing of  $\text{Bi}_2\text{O}_3$ ,  $\text{CuO}$ ,  $\text{CaCO}_3$ , and  $\text{SrCO}_3$  by thoroughly grinding the starting materials. This was followed by pressing into a pellet and sintering at  $880^\circ\text{C}$  (sample 1), doping with  $\text{SnO}$  and  $\text{SnO}_2$ , pressing into a pellet, sintering at  $880^\circ\text{C}$ , and annealing at  $950^\circ\text{C}$  for 15 minutes (sample 2), pressing into a pellet, and sintering at  $820^\circ\text{C}$  (samples 3 and 4). All materials were sintered and annealed in air in a muffle furnace. The ratios of the starting materials are given in Table 1.

TABLE I Molar ratios of starting materials

Sample	Bi-Sn-Ca-Sr-Cu molar ratios
1	2-0-1-2-2
2	2-1-1-2-2
3	1-0-1-1-2
4	2-0-1-2-2

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### Magnetic Measurements

Quantitative magnetic measurements were made using a vibrating sample magnetometer equipped with a continuous flow cryostat. The samples were cooled in zero field (ZFC) to 4.2K, and the diamagnetic shielding data was collected past the transition temperature in a field of 50 Oe. The sample was then field cooled (FC) through the transition temperature in order to monitor the Meissner effect. The density of the samples was measured and volume susceptibilities were determined. All data was corrected for demagnetization effects.

### Resistance Measurements

Resistance measurements were made from 20-300K utilizing an in-line four-probe technique. Compensation for the Seebeck effect was made.

### Surface Analysis

The surface, microstructure, and stoichiometry of the superconducting ceramics were determined by Rutherford backscattering (RBS) and scanning electron microscopy - energy dispersive X-ray analysis (SEM-EDX). A standardless semi-quantitative analysis program was used to determine the elemental analysis of the bulk material as well as that of the individual grains.

## RESULTS AND DISCUSSION

### Transition Temperature and Superconducting Volume Fractions

The magnetic data for the four samples studied show

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relatively broad transitions, indicative of the multiphase nature of the samples. Sample 1 displayed the greatest volume fraction of superconducting material, with 8.4% bulk diamagnetism in the Meissner signal and 13.1% for the maximum diamagnetic shielding. The  $T_c$  for sample 1 was monitored by both resistance and magnetic measurements. The onset temperature of the decrease in resistance was 87K, with zero resistance being realized at 37K. The magnetic data determined the  $T_c$  to be 77.6K for the ZFC run and 79.5K for the FC data set. The anomalously low temperature necessary for zero resistance is most probably due to contact problems or the percolative nature of the superconductivity. The results of the critical temperatures and diamagnetic fractions are summarized in Table II.

#### Surface Analysis and Microstructure

RBS of samples 1 and 2 yielded valuable information concerning the constitution of the sample surface. The surface stoichiometries (Bi-Sn-Sr-Ca-Cu) were determined to be (1:0.0:0.7:1.0:1.5) and (1:0.53:1.27:0.93:1.33) respectively. This data indicates that the surface is rich in Ca and Cu, with the latter probably being present in the form of oxides.

An EDX elemental analysis of sample 1 yielded a stoichiometry of  $\text{Bi}_{1.43}\text{Sr}_{1.62}\text{Ca}_{0.61}\text{Cu}_{2.00}$  and the SEM showed the material to be very porous with little or no melting. Analysis of single grains confirmed the multiphasic nature of the composite, however some grain of different morphology displayed very similar stoichiometries.

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TABLE II Transition temperatures and percent bulk diamagnetism

Sample	$T_C$ (ZFC)	$T_C$ (FC)	$T_C$ (onset)	$T_C$ (zero)	% (ZFC)	% (FC)
1	77.6	79.5	87	37	13.1	9.4
2	72.3	76.9	88	61	8.2	1.6
3	69.5	72.7	--	--	5.6	4.1
4	73.5	73.5	--	--	1.0	0.7

The overall stoichiometry of sample 2 was  $\text{Bi}_{0.61}\text{Sn}_{0.55}\text{Sr}_{1.28}\text{Ca}_{0.90}\text{Cu}_{2.00}$ . Analysis of single grains showed large areas of Sr depletion. As in the case of sample 1, no melting was observed and the individual grains were of widely differing morphology and composition.

Sample 3 was very homogeneous and individual grains had stoichiometries similar to that of the bulk ( $\text{Bi}_{1.50}\text{Sr}_{0.91}\text{Ca}_{1.07}\text{Cu}_{2.00}$ ). However, we did find areas heavily depleted in Bi, Sr, and Ca. In contrast to the previous ceramics, SEM showed some melting had occurred resulting in partial fusion of the grains in an annealed pellet. Analysis of some unannealed sintered powder yielded some lamellar grains of composition  $\text{Bi}_{1.7}\text{Sr}_{1.4}\text{Ca}_{0.9}\text{Cu}_{2.0}$ .

EDX of the final sample indicated severe Ca depletion. The sample was polycrystalline and very homogeneous (1 $\mu$  dia.). As in the case of the first two ceramics, the pressed pellet was very porous.



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#### CONCLUSIONS

The samples studied were generally multiphase in nature and very porous. The transition temperatures were found to be dependent on the molar ratios of the starting materials and firing conditions, but generally, the T<sub>c</sub>'s correspond to the 80K phase. More intimate mixing of the precursors must be obtained in order to increase the homogeneity of the fired material and increase the yield of the superconducting fraction. It may be that the best reaction conditions for the highest yields occur in a very narrow temperature range, requiring precise control of the firing temperature.

#### REFERENCES

1. a) Z. Z. Sheng and A. M. Hermann, Nature, **332**, 55 (1988).  
b) Z. Z. Sheng and A. M. Hermann, Nature, **332**, 138 (1988).
2. a) H. Takahi, H. Eisaki, S. Uchida, A. Maeda, S. Tajima, K. Uchinodura and S. Tanaka, Nature, **323**, 236 (1988).  
b) R. M. Hazen, C. T. Prewitt, R. J. Angel, N. L. Ross, L. W. Finger, C. G. Hadidiacos, D. R. Veblen, P. J. Heaney, P. H. Hor, R. L. Meng, Y. Y. Sun, Y. Q. Wang, Y. Y. Xue, Z. J. Huang, L. Gao, J. Bechtold, and C. W. Chu, Phys. Rev. Lett., **60**, 1174 (1988).

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